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Oxidative addition of alkenyl and alkynyl iodides to a Au(I) complex

Jamie A. Cadge, Hazel A. Sparkes, John F. Bower* and Christopher A. Russell*

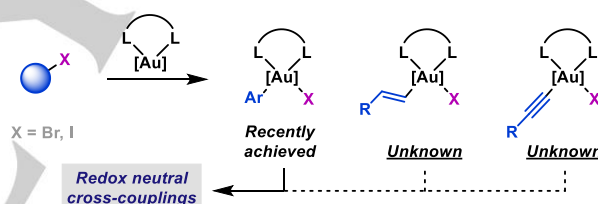
Abstract: The first isolated examples of intermolecular oxidative addition of alkenyl and alkynyl iodides to Au(I) are reported. Using a 5,5'-difluoro-2,2'-bipyridyl ligated complex, oxidative addition of geometrically defined alkenyl iodides occurs readily, reversibly and stereospecifically to give alkenyl-Au(III) complexes. Conversely, reversible alkynyl iodide oxidative addition generates bimetallic complexes containing both Au(III) and Au(I) centers. Stoichiometric studies show that both new initiation modes can form the basis for the development of C–C bond forming cross-couplings.

Significant recent progress has been made in demonstrating elementary cross-coupling steps at Au-centers.^[1] Bourissou, Amgoune and co-workers and our group have shown that Au(I)-systems modified with appropriate ligands are effective for hitherto unknown Ar–X (X = I, Br) oxidative additions.^[2–4] In addition to these thermal pathways, significant progress has also been made in oxidative addition at gold using photochemically activated routes.^[5,6] In part, such oxidative addition steps are challenging^[7] because of the high energy barrier associated with the Au(I)/Au(III) redox couple (E_{red}° : Au^{III/I} = 1.41 V vs Pd^{II/0} = 0.92 V).^[8] Catalysts that can overcome this are significant because they dispense with the highly reactive external^[9] or internal^[10] oxidants typically required in Au-mediated cross-couplings. Indeed, using Ar–X oxidative addition as a platform, redox neutral Au-based aryl C–H arylations and Negishi-like cross-couplings have now been achieved.^[3,4] In these studies, *reversible* Ar–X oxidative addition was faster for more electron rich arenes, offering a counterpoint to the electronic trends typically seen in Pd-based processes.^[2–4] Accordingly, new Au-mediated C–X oxidative additions are not merely of interest from a reactivity viewpoint but also have significant potential for addressing broader selectivity challenges in cross-coupling chemistry.

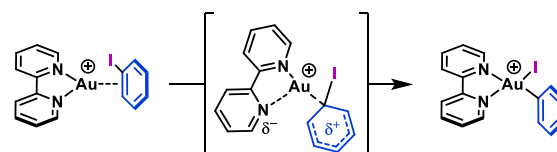
Fundamental to the endeavors outlined above is the detailed insight into the oxidative addition step provided by stoichiometric studies (Scheme 1A). The underpinning feature of Au-systems that are effective for Ar–X oxidative addition is the use of bidentate ligands, namely a carboranyl diphosphine (Bourissou & Amgoune),^[2] a hemilabile *P,N*-system (Bourissou & Amgoune),^[3a,c] and 2,2'-bipyridine (our group, Scheme 1B).^[4] These enforce sufficient changes to the properties of the Au-center to allow Ar–X oxidative addition. However, the generality of this tactic for other classes of C–X bond has not been

determined, and, to the best of our knowledge, there are no isolated examples of intermolecular Au-mediated oxidative addition of either alkenyl or alkynyl-halides, although, encouragingly, such steps have been invoked in recent reports of gold catalyzed processes utilizing either alkynyl iodides or alkynyl bromides.^[11] The feasibility and nuances of such processes are therefore inherently uncertain, especially given the unusual mechanistic traits of Ar–X oxidative additions, where initial electron donation from the arene to the Au(I) center was found to be a key feature (Scheme 1B). In this report, we show that Au(I)-complexes can indeed be induced to undergo intermolecular oxidative addition of alkenyl C(*sp*²)–I and alkynyl C(*sp*)–I bonds, and that, significantly, the former are stereospecific (Scheme 1C). We also show that these processes can be integrated into cross-couplings, setting the stage for the long-term development of catalytic variants.

(A) Oxidative addition of organohalides to Au(I):^[4]

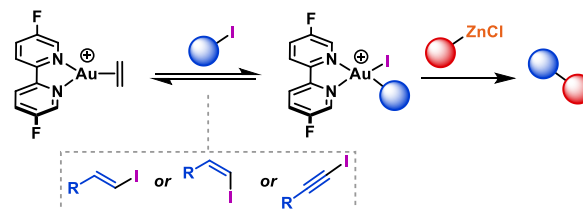


(B) Initial electron donation from the aryl iodide to Au(I):



Key mechanistic feature of Ar–X oxidative additions

(C) New classes of oxidative addition - *sp*² and *sp* centers (this work):



Scheme 1.

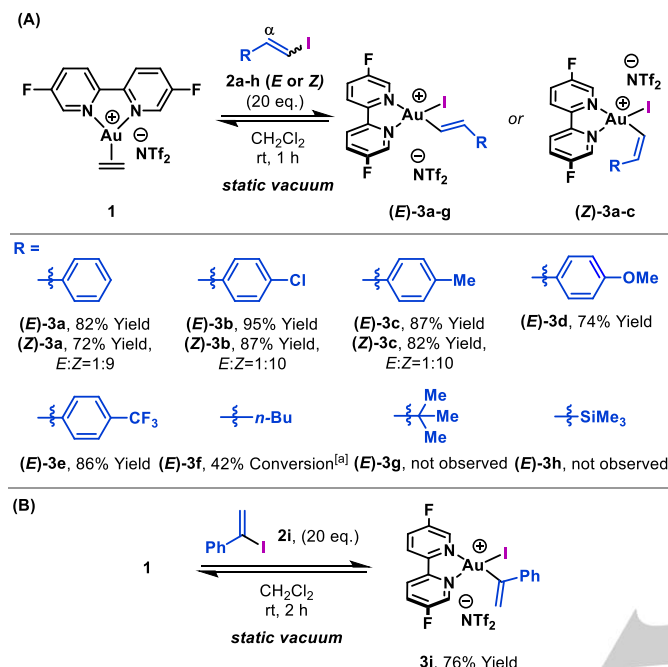
Our studies to explore the feasibility of alkenyl C(*sp*²)–I oxidative addition began by examining 5,5'-difluoro-2,2'-bipyridyl gold(I) ethylene complex **1** (Scheme 2A).^[4] As evidenced by spectroscopic analysis of the ethylene unit, the narrow bite angle (75°) bipyridyl ligand leads to significant back donation to the co-

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ligand, a feature that is desirable for promoting oxidative addition. Reaction of **1** with iodostyrene (**E**-**2a**) under static vacuum^[12] gave a bright yellow solution whose analysis by ¹⁹F NMR spectroscopy revealed two new multiplets (1:1 ratio), indicating desymmetrization of the Au-complex, and mass spectrometry



Scheme 2. Oxidative addition of alkenyl iodides. [a] Conversion by ¹⁹F NMR after heating at 50 °C for 2 h.

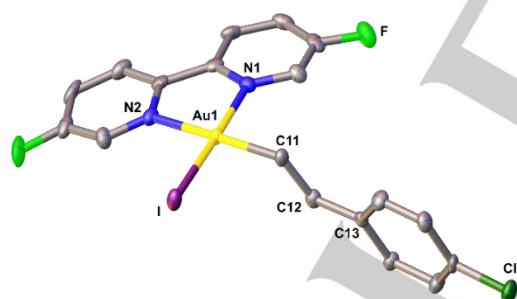
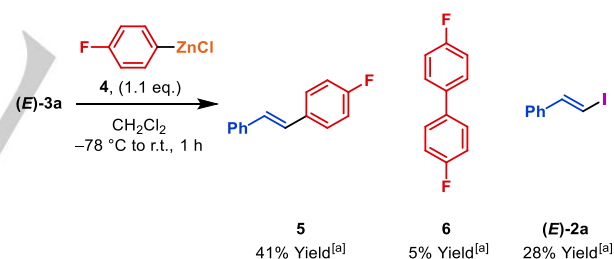


Figure 1. Thermal ellipsoid plot (50% probability level) of (**E**-**3b**; counterion and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): N1-Au1 2.081(3), N2-Au1 2.119(4), N1-Au1-N2 78.65(14), Au1-I 2.5370(3), Au1-C11 2.007(4), Au1-C11-C12 120.6(3).

(ESI⁺) gave *m/z* 618.9754 (calcd. 618.9757, [M-NTf₂]⁺). These observations, as well as other data (see SI), are consistent with oxidative addition to give Au(III) complex (**E**-**3a**).^[13] When a solution of (**E**-**3a**) was exposed to an atmosphere of ethylene reversal to starting complex **1** was observed, demonstrating the reversibility of oxidative addition.^[12] Similar behavior was observed for *p*-substituted variants (**E**-**2b-e**). The structure of (**E**-**3b**) was confirmed by single crystal X-ray crystallography, which revealed a distorted square-planar geometry (Figure 1). Non-styrenyl alkenes do not readily participate, e.g., oxidative addition

with (**E**-**2f** (R = *n*-Bu) to form (**E**-**3f**) was sluggish, even at 50 °C, whereas (**E**-**2g**) and (**E**-**2h**) did not provide (**E**-**3g**) and (**E**-**3h**). Oxidative addition of α -iodostyrene **2i** was efficient and reversible, giving Au(III) complex **3i** in 76% yield (Scheme 2B). The fluorine atoms of **1** were included as a reporter nucleus (¹⁹F NMR); similar results were obtained using 2,2'-bipyridine as ligand (see SI).

Relative initial rates were determined for the formation of (**E**-**3a, d** and **e**) (see SI). Compared to parent (**E**-**2a**) (*k*_{rel} = 1.0), the *p*-OMe analogue (**E**-**2d**) gave a higher rate of oxidative addition (*k*_{rel} = 1.8), whereas electron poor *p*-CF₃ analogue (**E**-**2e**) reacted more slowly (*k*_{rel} = 0.02). This trend mirrors observations made previously with aryl iodides,^[4] and indicates that initial electron donation from the vinyl unit to the Au center is a key factor. One explanation is that an electron donating R-group is better able to stabilize developing positive charge at the α -carbon of the alkene during oxidative addition (*cf.* Scheme 1B). An alternate explanation is that electron rich alkenes facilitate displacement of ethylene from **1** to give a new π -complex *in advance* of oxidative addition. At atmospheric pressure, ¹⁹F NMR profiling of the formation of (**E**-**3d**) revealed the rapid disappearance of **1** (δ_F = -127.2 ppm) to give an intermediate (δ_F = -121.8 ppm) *en route* to the product; this intermediate is most likely the Au- π -complex of (**E**-**2d**).^[14] When **1** was exposed to *tert*-butyl vinyl iodide (**E**-**2g**) under analogous conditions, a similar intermediate formed, albeit to a lesser extent, indicating that displacement of ethylene still occurred, even though conversion to (**E**-**3g**) was not observed. Overall, these observations indicate that oxidative addition, rather than displacement of ethylene from **1**, is the more demanding step and that the alkenyl iodide must have the correct properties to facilitate this.

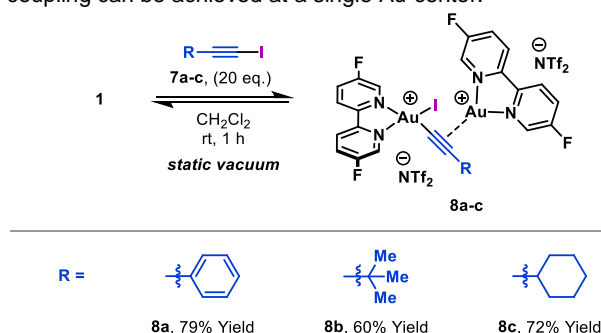


Scheme 3. Transmetalation and reductive elimination from (**E**-**3a**). [a] Determined by GC analysis.

Based on the above, the stereospecificity of oxidative addition with respect to alkenyl iodide geometry was uncertain: if a substantial buildup of positive charge occurs at the α -carbon then scrambling of stereochemistry might ensue due to the diminished double bond character. Accordingly, oxidative addition studies were undertaken using (**Z**-**2a-c**). In the event, Au(III) complexes (**Z**-**3a-c**) were formed in 72-87% yield and with transfer of alkenyl iodide stereochemistry (*Z*:*E* >9:1). Accordingly, the process is diastereospecific, such that the geometry of the alkenyl iodide determines the geometry of the alkenyl ligand of the Au(III) complex. This feature is analogous to the synthetically valuable diastereospecificity observed for oxidative addition of alkenyl halides to Pd(0) complexes.^[15,16] To validate subsequent C-C bond formations, (**E**-**3a**) was exposed *p*-FC₆H₄ZnCl **4** and this generated **5** in 41% yield (Scheme 3). Alkenyl iodide (**E**-**2a**,

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resulting from C–I reductive elimination, was observed in 28% yield, along with small quantities of homocoupling product **6**. Accordingly, transmetalation and C–C reductive elimination are feasible, such that all steps of a conventional Negishi cross-coupling can be achieved at a single Au-center.



Scheme 4. Oxidative addition of alkynyl iodides.

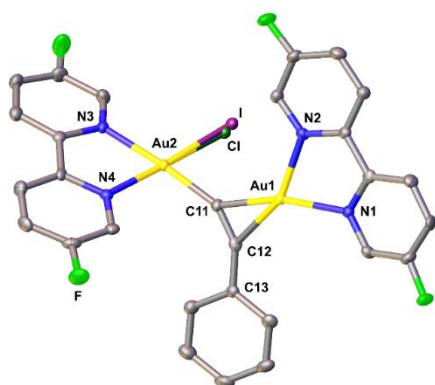
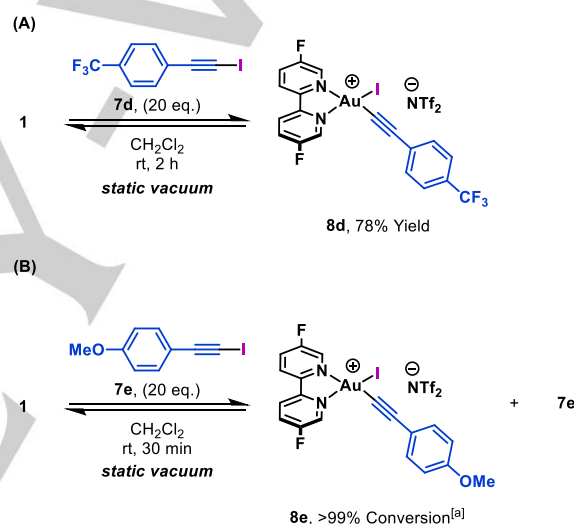


Figure 2. Thermal ellipsoid plot (50% probability level) of **8a** with H atoms, the counterion and solvent of crystallization omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–Au1 2.169(3), N2–Au1 2.172(3), N1–Au1–N2 75.62(11), C11–Au1 2.029(4), C12–Au1 2.089(4), C11–C12 1.261(5), C11–C12–C13 150.5(4), Au2–C11–C12 149.0(3), C11–Au2 1.976(4), I–Au2 2.5752(4), Cl–Au2 2.241(6), N3–Au2 2.089(3), N4–Au2 2.080(3), N3–Au2–N4 79.75(12). The structure contains disordered Cl/I atoms (I/Cl 0.78/0.22 occupancies respectively), as observed with similar complexes.^[2,17]

Next, the feasibility of oxidative addition at *sp*-centers was explored by exposing **1** to various alkynyl iodides (Scheme 4). Under static vacuum, reaction of phenyliodoacetylene **7a** with **1** generated a bright orange solution, and complete conversion was verified by ^{19}F NMR spectroscopy. Three new signals were observed (1:1:2 ratio), consistent with the presence of two Au-centers, one of which has been desymmetrized. A similar outcome was observed at -20°C , whereas higher reaction temperatures led to decomposition. Mass spectrometric analysis (ESI⁺) gave m/z 616.9599, which corresponds to the initially expected oxidative addition product (calcd. 616.9601, $[\text{M}-\text{NTf}_2]^+$). Ultimately, the structure of the new species was confirmed by single crystal X-ray crystallography, which revealed a mixed valence digold complex **8a**, where C–I oxidative addition has occurred at one Au-center and the other is π -bound to the alkynyl unit (Figure 1). This result compliments the impressive body of results where digold species, typically with both metal centers in the +1 oxidation state, have been shown to be pivotal in dual

activation gold catalysis.^[18] The Au(III) center of **8a** has a distorted square-planar geometry; the Au(I) center is symmetrically bonded to the F_2 -bipy unit and asymmetrically bonded to the alkyne {8% slippage towards C(11)}. The C=C unit bonded to the Au(I) center is lengthened {1.261(5) Å} and the Ph substituent of this unit is bent back to $150.5(4)^\circ$. These data deviate more strongly from those of a free alkyne in comparable cationic complexes containing 2-coordinate gold for which the limited pool of X-ray data show bond distances that average 1.21 Å and C=C–C bend back angles that average 168° .^[19, 20] The more pronounced deformation of the acetylide unit in **8a** is consistent with previous observations that 3-coordinate cationic Au(I)-complexes express enhanced π -back-donation compared to their 2-coordinate counterparts.^[4,21] Related bimetallic species, containing both σ - and π -bound Au-centers, have been generated previously by distinct methods.^[22] A complex similar to **8b** can also be formed using 2,2'-bipyridine as the ligand (see SI).



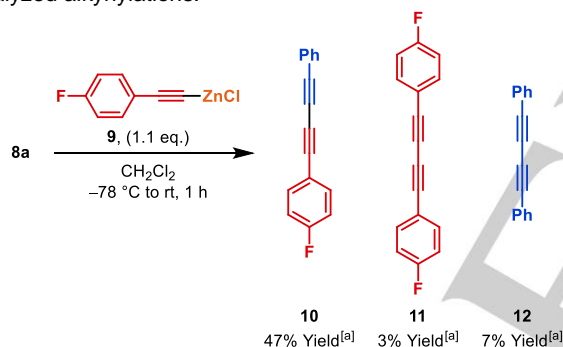
Scheme 5. Electronic effects on the oxidative addition of alkynyl iodides. [a] Conversion by ^{19}F NMR analysis (isolated as a mixture of **8e** and **7e**).

When a CH_2Cl_2 solution of **8a** was pressurized with ethylene (1 bar) complete conversion to **1** was observed, demonstrating once again the reversibility of C–I oxidative addition. Monitoring of the forward process (**1** to **8a**) by ^{19}F NMR spectroscopy revealed initial conversion to an intermediate, symmetrical complex, which was tentatively assigned as the Au- π -complex of phenyliodoacetylene **7a**. *tert*-Butyl and cyclohexyl systems, **7b** and **7c**, behaved similarly, providing **8b** and **8c** in 60% and 72% yield (Scheme 4). Interestingly, distinct outcomes were observed for *p*- CF_3 and *p*-OMe substituted systems **7d** and **7e**. For the former, conversion to monometallic complex **8d** occurred and a bimetallic complex (cf. **8a**) was not observed (Scheme 5A). Here, the electron poor alkynyl unit of **8d** is presumably a weaker ligand for Au(I) such that competing π -complexation is not thermodynamically favored. Compared to parent system **7a**, the initial rate of oxidative addition with **7d** was also much slower (see SI). By contrast, *p*-OMe substituted system **7e** underwent oxidative addition faster, and, perhaps surprisingly, also delivered a monometallic complex (**8e**) (Scheme 5B). Signals consistent

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with alkynyl iodide **7e** were also observed. We suggest that the relatively electron rich alkyne of **7e** can displace Au(I) from any initially formed bimetallic species. The observed trends in the rates of oxidative addition indicate that charge stabilization in the transition state is once again a key factor (*cf.* Scheme 1B).

Reaction of **8a** with alkynyl-zinc reagent **9** delivered coupling product **10** in 47% yield; homocoupled products **11** and **12** also formed in 3% and 7% yield, respectively.^[23] Other classes of organometallic nucleophile resulted predominantly in homocoupling products (see SI). The origin of this side process was investigated using an analogue of **8a** derived from ¹³C-labelled phenyliodoacetylene (see SI). ¹³C NMR profiling of a representative cross-coupling revealed the immediate formation of alkynyl iodide **7a**, providing direct evidence for C–I reductive elimination under the reaction conditions. The formation of homocoupled products then ensued, and these increased over a week, suggesting that their formation is promoted by decomposition products of the Au-complex. Hashmi and co-workers have developed catalytic C–C bond formations where alkynyl-Au(III) species were generated by C–I cleavage; these processes did not proceed via formal C–I oxidative addition and required highly reactive alkynyl-iodine(III) reagents.^[20c] The present study suggests that more available and atom economical alkynyl-iodine(I) precursors can form the basis for future Au-catalyzed alkynylations.^[24]



Scheme 6. Transmetalation and reductive elimination from **8a**. [a] Determined by GC analysis.

In summary, we show for the first time that modification of the ligand environment at Au can be exploited to allow oxidative addition of alkenyl and alkynyl iodides.^[25] These processes display an important electronic trend wherein more electron rich substrates engage in more facile oxidative addition. For alkenyl iodides, diastereospecific oxidative addition occurs, and, going forward, this offers a key stereocontrol element. For alkynyl-based systems, electronically dependent generation of mono- or bi-metallic complexes is observed. Both new initiation modes can be integrated into C–C bond forming sequences that harness key steps typical of Pd-catalysis. The challenge of using readily available internal oxidants for Au(I)→Au(III) redox cycles is well recognized as a major impediment to realizing Au-catalyzed C–C/C–X bond formations. Our studies address this at a fundamental level, providing valuable insight that should enable further development of the area.^[26]

Acknowledgements

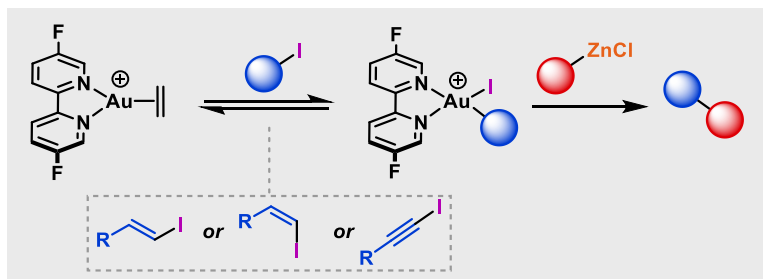
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Keywords: gold • oxidative addition • alkenyl iodide • alkynyl iodide • bipyridyl

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- [23] Exposure of **8a** to $p\text{-FC}_6\text{H}_4\text{ZnCl}$ delivered the expected Negishi-type product in 14% yield (see SI).
- [24] During the preparation of this manuscript a process invoking photosensitized oxidative addition of alkynyl iodides to Au(I) was reported: Z. Xia, V. Corcé, F. Zhao, C. Przybylski, A. Espagne, L. Jullien, T. Le Saux, Y. Gimbert, H. Dossmann, V. Mouriès-Mansuy, C. Ollivier, L. Fensterbank, *Nature Chem.* **2019**, *11*, 797.
- [25] Analogous processes with allyl iodide resulted in competing *N*-allylation of the bipyridyl ligand. Alkenyl/alkynyl bromides are not suitable electrophiles.
- [26] Efforts to develop catalytic variants are ongoing. We suggest the key impediment is the fragility of the [(bipy)Au]⁺ complex that is generated upon C–C reductive elimination.

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alkynyl iodides to a Au(I) complex